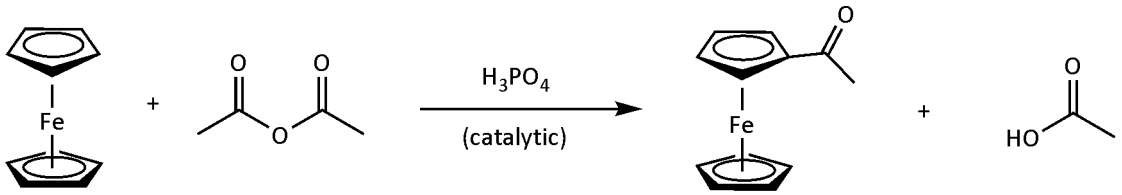
Friedel-Crafts Acylation. Acetylation of Ferrocene.

Reading Read about the molecules ferrocene and acetylferroene on-line. See also, Klein *Organic Chemistry* 3rd edition, Section 18.6 regarding the Friedel-Crafts reaction.

Overview

In this experiment you will perform a Friedel-Crafts acylation of an electron-rich aromatic system (each five-membered ring can be considered a cyclopentadienyl anion). The product will be purified by column chromatography, a *very* common method of purification.



Prelab

Be sure to include in your notebook your **Name**, **Date**, **Title**, **Purpose**, **Chemical Reaction**, a completed **Reagent Table** (see procedure below for amounts), and a brief **Outline** of the procedure. Find and record in your notebook the melting point of ferrocene [a.k.a., di(cyclopentadienyl) iron(II)], acetylferrocene, and diacetylferrocene (a potential side product). Make sure that you calculate your theoretical yield of acetylferrocene *before the laboratory*.

Procedure

Combine 0.93 grams of ferrocene, 5 mL of acetic anhydride, and 1 mL of 85% phosphoric acid in a Pyrex test tube. Stir the mixture well then heat it in a 60-80°C water bath for 45 minutes. Pour the mixture into a 250-mL beaker that contains approximately 6 grams of ice. Use 5 mL of DI water in portions to transfer any of the mixture that remains in the test tube. While stirring with a glass stir rod, slowly add 30 mL of 3.0 M NaOH. Continue stirring until all the ice is melted. Check the pH and if less than pH 5, then add small portions of solid sodium bicarbonate until the solution is neutral (*Caution*, frothing is possible!).

Isolate the crude product by *vacuum* filtration – use a Büchner funnel. Use a small amount of ice-cold DI water to transfer the remaining contents of the beaker. Wash the solid product with 5 mL of DI water and air-dry under vacuum for ~2 minutes. Transfer your product (and weighing paper) to a small beaker and dry your product as described below. (you do not need to weigh the product at this point.)

Transfer the sample to a 50 mL Erlenmeyer flask and dissolve your crude product in 10 mL of methylene chloride. Dry the solution with sodium sulfate (Na_2SO_4). Let the solution sit over the Na_2SO_4 for ~15 min, then decant into a clean dry 50 mL round-bottom flask and remove the methylene chloride using the rotary evaporator.

Perform a TLC analysis of your crude product. Dissolve 1-2 mg of your crude product in ~0.5 mL of methylene chloride and do the same for a sample of pure ferrocene. Spot both samples on one TLC plate with a co-spot in the middle and develop the plate using methylene chloride. Determine the R_f of all visible spots. Record these values and an "exact" picture of the TLC plate in your notebook.

During the next laboratory period, find the weight of your dried product and note its physical appearance (solid, oil, color, etc.). Calculate the *crude* yield of your product (after the chromatography of a portion of your product you will calculate a *purified* yield).

Packing the column. The Slurry Method.

Prepare a chromatography column by placing a small plug of cotton in the bottom of the provided column. Clamp the column on a ring stand (with a burette clamp) and cover the cotton plug with ~1 cm of sand. Fill the column with ~ 5 mL of petroleum ether (pet. ether, see note below). Drain just enough of the solvent to wet the sand and cotton plug. In a small beaker, weigh out 4-5 g of silica gel (***Avoid generating too much silica gel dust: It is an irritant and is hazardous to the lungs. Pour slowly out of the container.***). To the silica gel, *in the hood* add ~20 mL of petroleum ether and swirl gently, just enough to form a thin slurry (the silica gel is much safer when wet with solvent). Using a small conical funnel (with a piece of wire for an air space), add the slurry to the column. Start draining the solvent from the column into a 50 mL Erlenmeyer flask or a small beaker. As the solvent drains from the column, the silica gel will begin to pack down. Tap the column with your fingers gently to help pack the silica gel. Reuse the solvent that drains off at the bottom to transfer all the silica gel from the beaker. Make sure that that there is always at least 1 to 1/2 cm of solvent above the top of the silica gel. ***Never let the level of the solvent dip below the level of the silica gel, otherwise you will have to start the column over.*** Cover the top of the packed silica gel with 1/2 - 1 cm of sand. Gently tap the side of the column with your fingers to level the layer of sand. Drain any remaining solvent in the column to just above the layer of sand. The column is now prepared.

(Note: Petroleum ether (aka Pet. ether) is not actually an ether, like diethyl ether. It's a mixture of low-boiling hydrocarbons and is available in different boiling-point ranges, in this case 40-60°C, Petroleum ether is sometimes also called Ligroin.)

Loading the sample:

Weigh out 300 mg of your crude acetylferrocene (~1/3 or your sample) and place it in a small clean test tube. Dissolve the sample in a minimum amount of methylene chloride (0.5 – 1.0 mL). Using a 9" glass Pasteur pipette (& bulb), transfer the solution to the top of the column by carefully introducing the solution down the inside wall of the burette. Rinse the test tube with another 0.5 mL of CH_2Cl_2 and add this to the column as before. Drain solvent from the column until the level of the solution is just touching the top of the sand layer. Add ~1 mL of petroleum ether, then drain down to the level of the sand. The sample is now loaded.

Elution:

Carefully fill the column with petroleum ether (~10 mL) and elute the column with petroleum ether. When the first colored band is just about to come off the column, replace the beaker or flask with a tared 125 mL Erlenmeyer flask. Continue eluting the column with 5 mL portions of petroleum ether until the first colored band comes completely off the column. (As the first band comes off, remove any formed solids from the tip of the column with a few drops of pure CH_2Cl_2) Then elute the column with 5 mL of 1:1 petroleum ether/ CH_2Cl_2 (to condition the column for CH_2Cl_2), then with pure CH_2Cl_2 in 5 mL portions until the next colored band comes off the column. Just before the second colored band comes off the column, switch to a new pre-weighed (tared) 50 mL flask and collect the second colored band. Remove the CH_2Cl_2 on the steam bath in the hood in the fume hood.

To Complete the Experiment – Partial Report

Weigh your product and calculate the percent yield of acetylferrocene. You will need to correct for only using 1/3 of your sample (see below). Determine the melting point of your crude and purified acetylferrocene. Obtain a ^{1}H NMR spectrum of your purified sample (see instructor).

Disposal: Once you have obtained all required data for your purified product, dissolve the material in the minimum amount of CH_2Cl_2 to transfer it to the labeled collection beaker in the hood. Transfer the remainder of your solid crude product similarly to the labeled collection beaker in the hood.

Include the following information in your partial report, the amount of your crude yield, the amount that you purified, the amount of acetylferrocene that you obtained, its physical properties (color, mp) and the calculated total percentage yield of acetylferrocene. In your conclusion, summarize the results from your experiment, including the analysis by TLC and purification by column chromatography, and answer the questions below.

Questions

1. Why is acetylation of acetylferrocene, which gives diacetylferrocene, faster on the unsubstituted cyclopentadienyl ring than it is on the one with the acetyl group?

2. What is the purpose of the phosphoric acid in this reaction?

Calculation of Percent Yield

To calculate the total yield of acetylferrocene, assume that the percent acetylferrocene you get from the purification is the same as in the crude product. To demonstrate this, consider the following results obtained by a student.

Crude yield of the acetylation reaction was 0.857 g
Weight of sample used for purification was 0.324 g
Weight of purified acetylferrocene obtained was 0.193 g

Percent of acetylferrocene in the sample is: $\frac{0.193g}{0.324g} \times 100 = 59.6\%$

Percent of acetylferrocene in the total crude product is: $(0.857g)(0.596) = 0.511g$

If the theoretical yield of acetylferrocene is 0.945 g (from the Prelab Reagent Table), then

Percent yield of acetylferrocene overall is: $\frac{0.511g}{0.945g} \times 100 = 54.1\%$